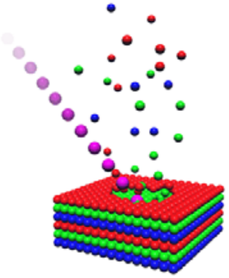


Advanced Inkjet Printing Technology for Trace Explosive Standards

Greg Gillen, Robert Fletcher, Jenny Verkoutern, Mike Verkouteren, Cindy Zeissler, George Klouda, Bruce Benner, Maria Santiago and Andrew Evans

Surface and Microanalysis Science Division
National Institute of Standards and Technology
Gaithersburg, MD 20899

Standards for Trace Detection

To support the NIST metrology program in trace explosives detection we need a variety of well defined standard materials. For example:

- Concentration standards for determination of IMS detection limits, linear response, day-to-day repeatibility. Need precise concentration standards over wide range. Need to prepare standards on wide variety of swipe materials.

- Operational standards – test swiping methodologies, portal testing materials.

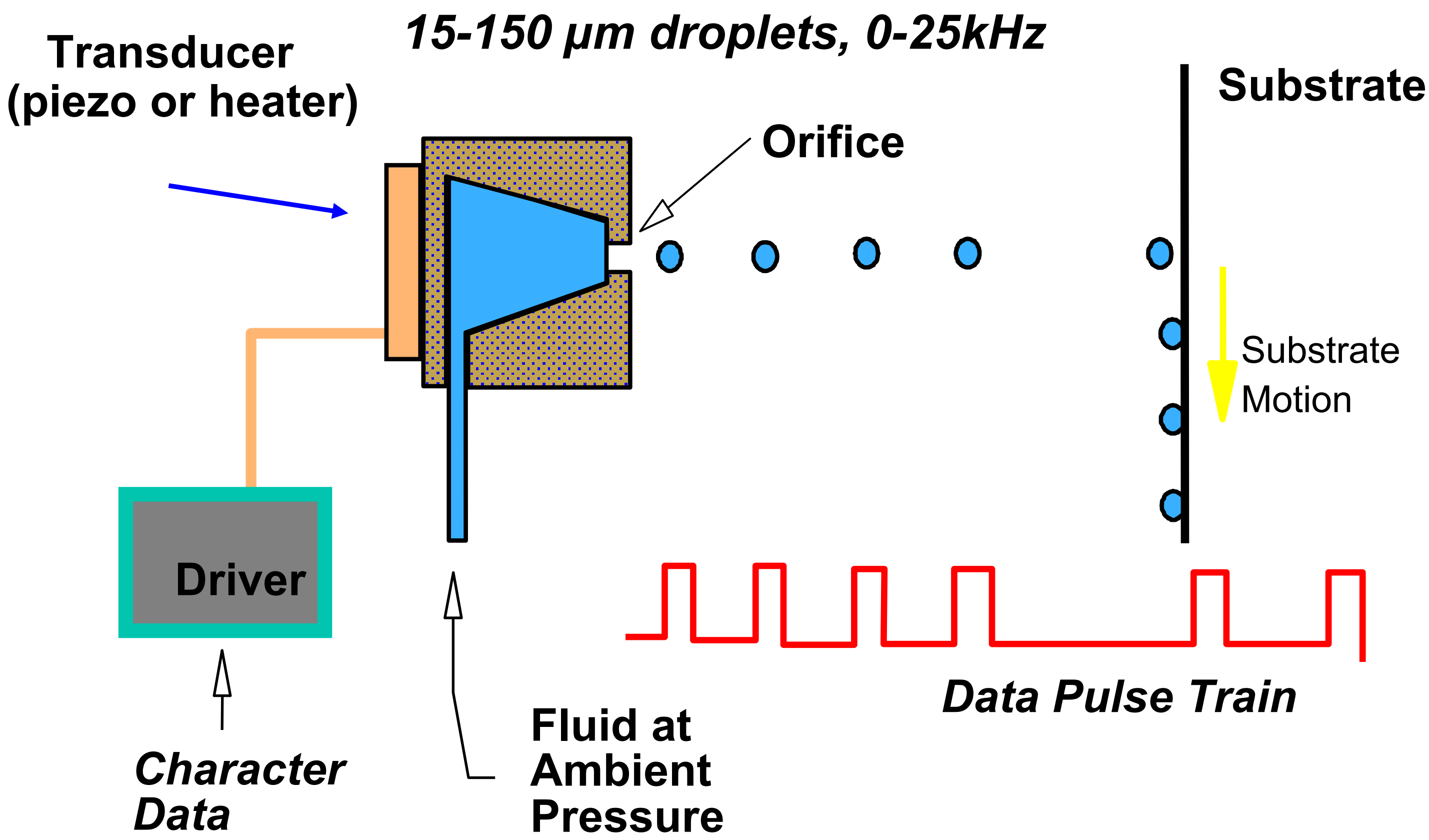
- Routine QA/QC standards

We are exploring drop-on-demand ink jet printing of explosives (and narcotics) as a possible solution.

Drop-on-Demand Inkjet Printing

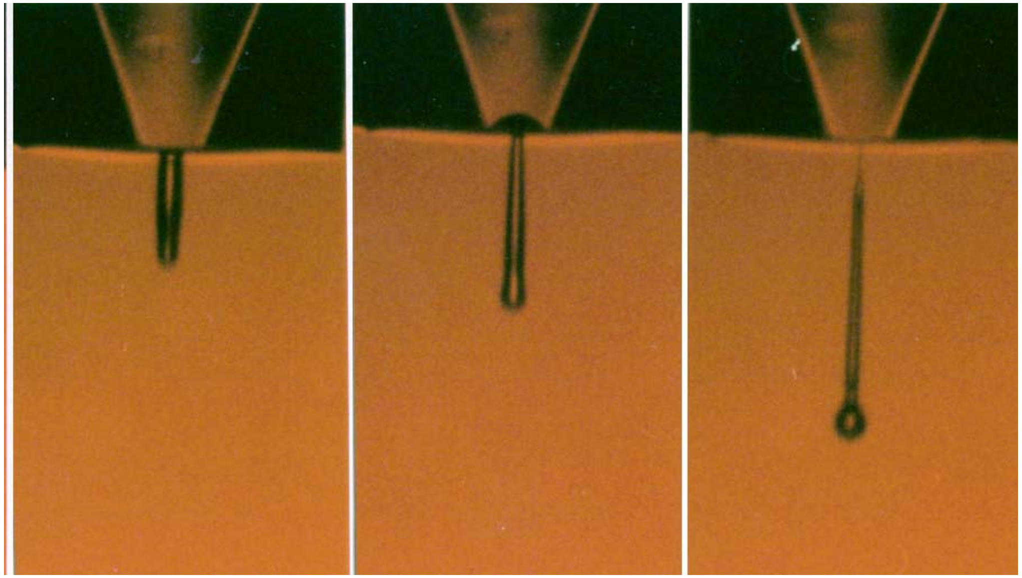
Advantages

- single drop delivery with each drop of known concentration
- vary concentration with # drops, large dynamic range (10^5)
- flexibility in compounds used (explosives, narcotics) and substrate
- rapid, reproducible, non-contact fluid delivery

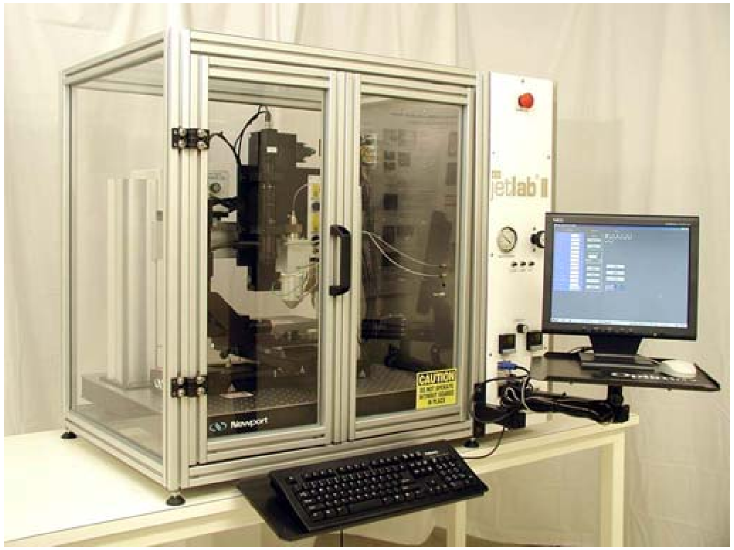


Physics of Drop-on-Demand

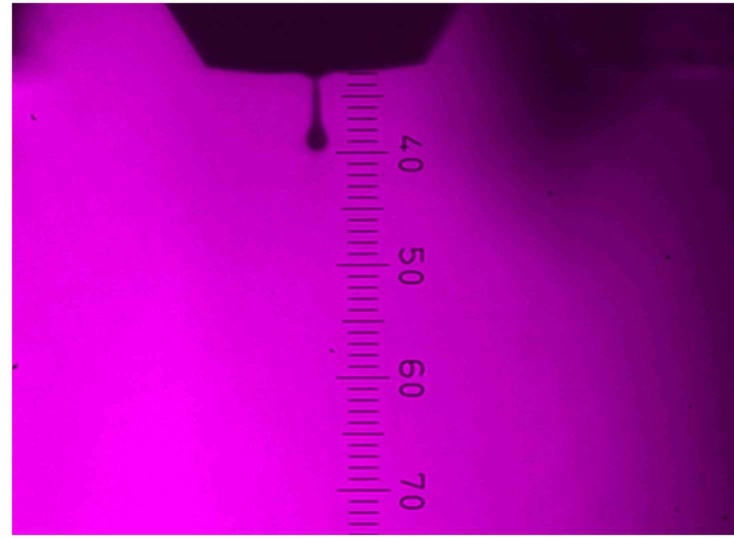
- Transducer imparts energy to fluid volume
- Acoustic waves propagate to orifice or free surface
- Energy converted from pressure to velocity at orifice (atmospheric pressure)



Trace Explosive Standards Using InkJet Printing Technology



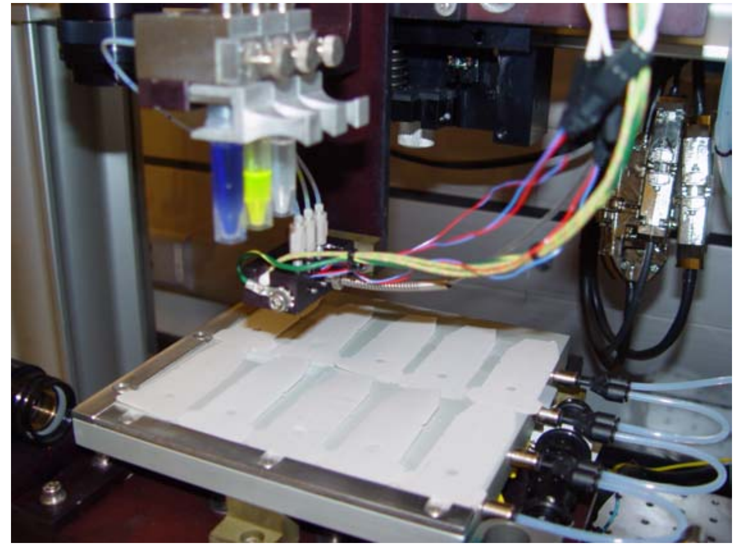
NIST JetLab II Printer System

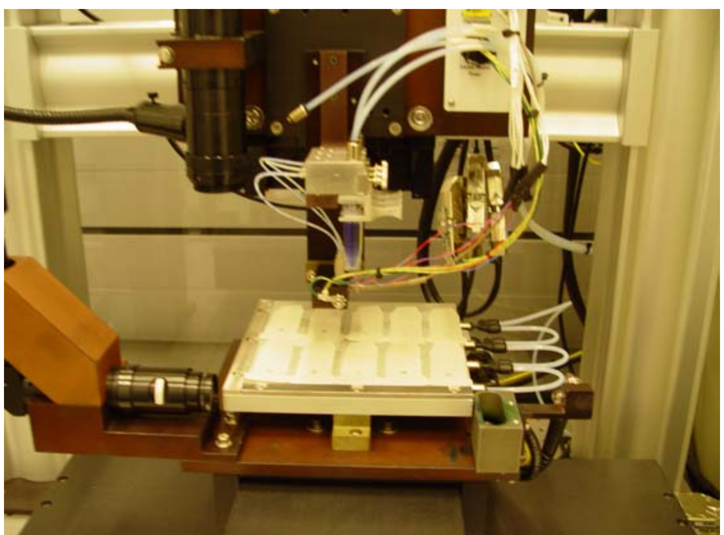


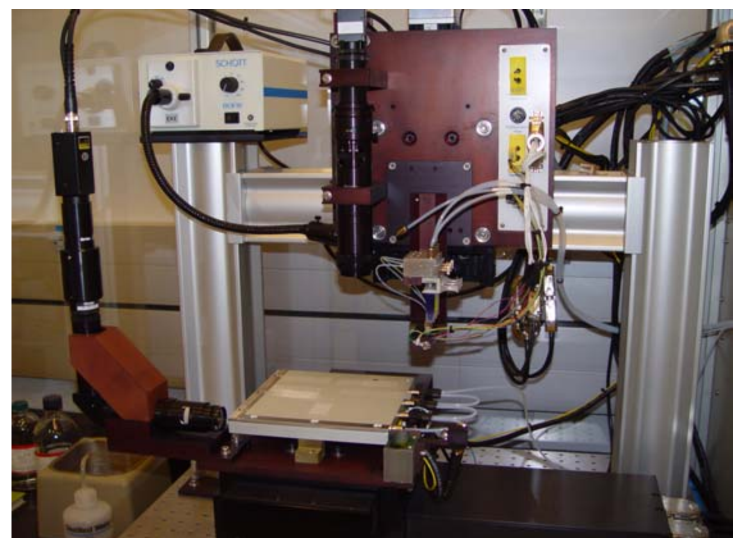
Isobutanol/RDX mixture being ejected from NIST inkjet print head

- Piezo electric print head.
- 4 independent fluid reservoirs/printheads
- 50 micrometer jet orifice
- Drop-on-demand, print-on-the-fly modes.
- Strobe illumination for visualization of droplet formation, high resolution sample viewing

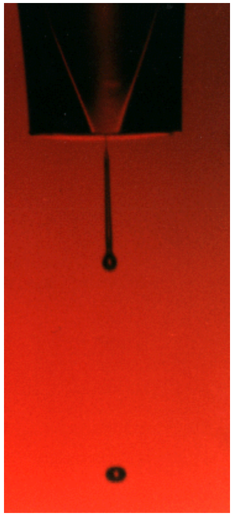
NIST JetLab Printer System







Feasibility Tests

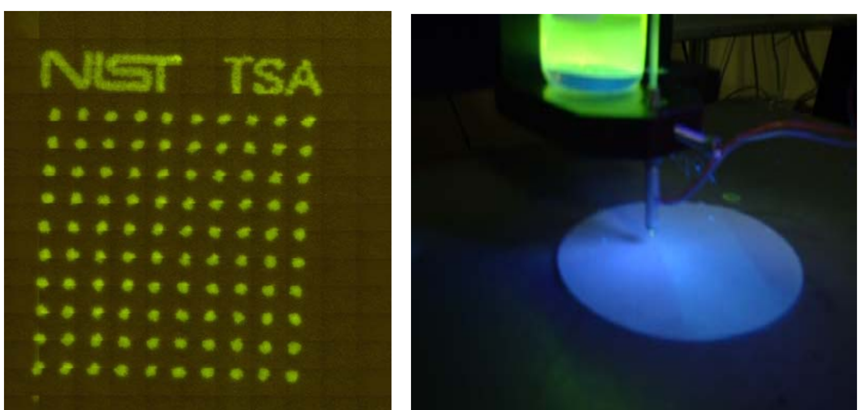


- Arrays containing trace levels of TNT and fluorescent dyes were jetted onto a variety of test surfaces using various solvents.

- Arrays characterized by optical and fluorescence microscopy and advanced surface analysis tools available at NIST.

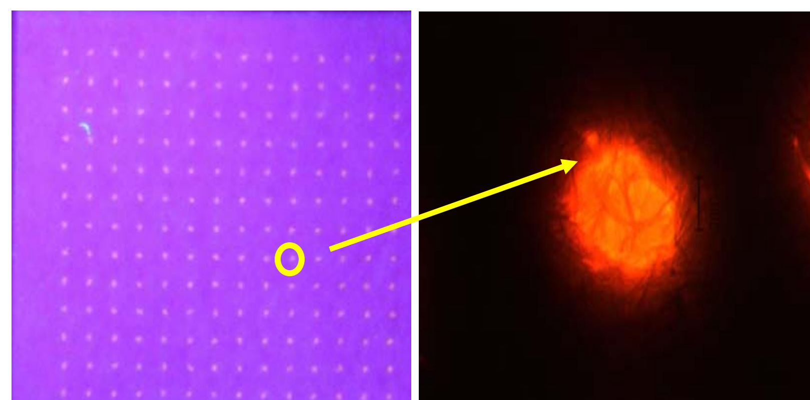
- Conclusion: Inkjet printing of explosives is feasible. Appropriate solvent and substrate selection critical.

Fluorescein + TNT



2.5 cm

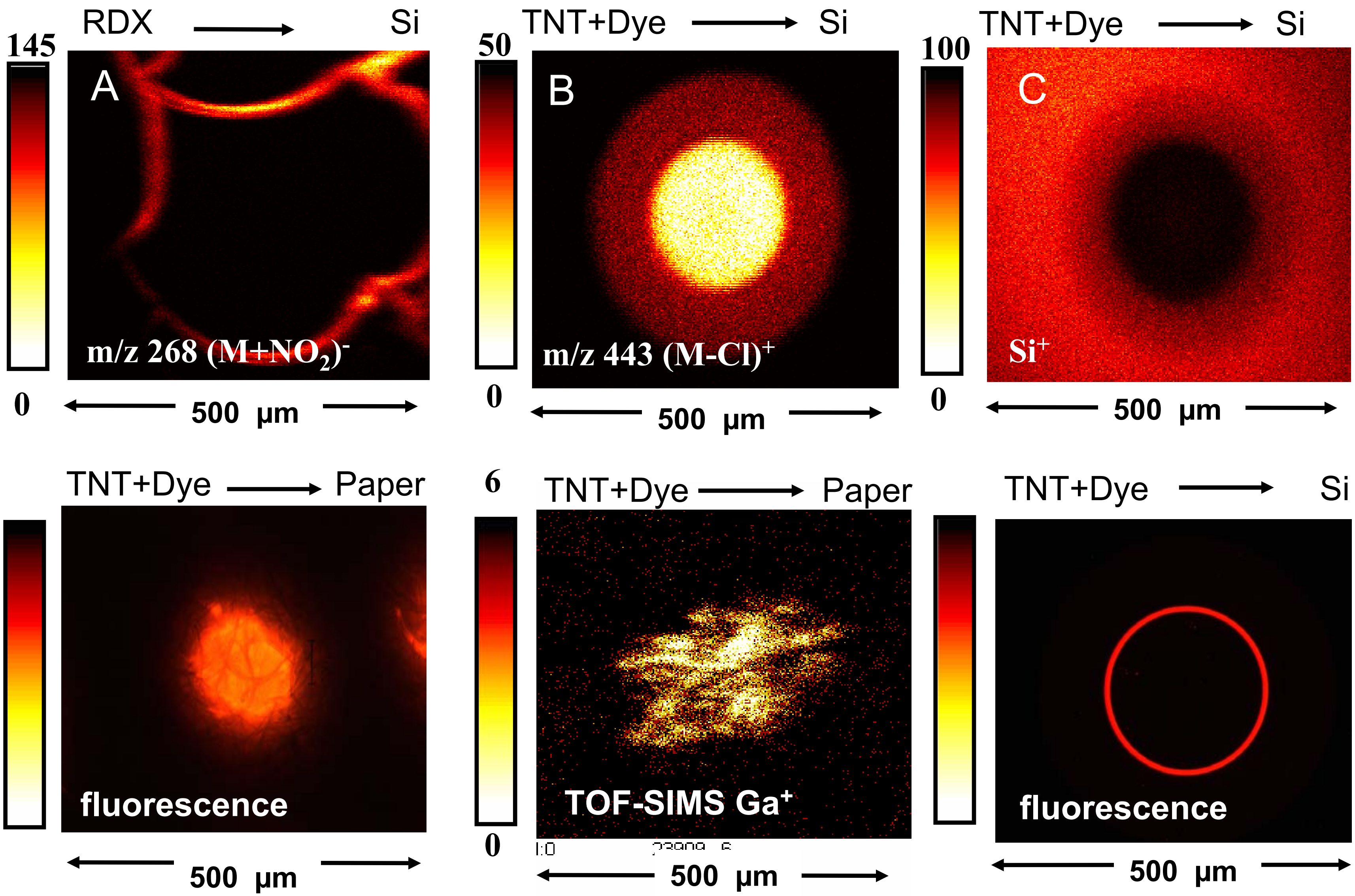
Rhodamine + TNT



2.5 cm

150 µm

Characterization of Inkjet Droplets



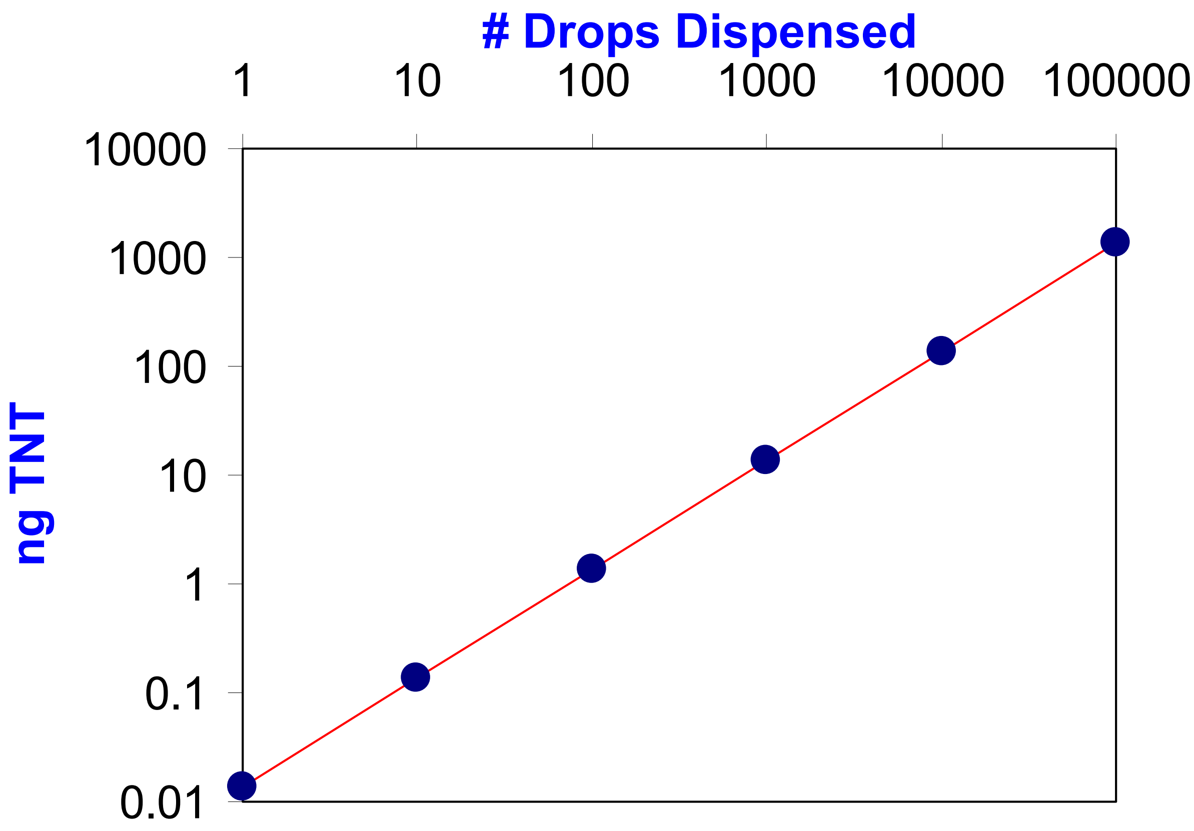
Explosive Standard Preparations

- Commercially available standards of TNT, RDX and PETN in acetonitrile (1.2 mL at 1 mg/mL, Cerilliant) was evaporated to near-dryness, dissolved in isobutanol, tranferred to a 10 mL volumetric flask, and diluted to the mark with isobutanol (nominal concentration = 120 μg/mL).

- For visualization of standards, some samples were doped with fluorescein or blue ink.

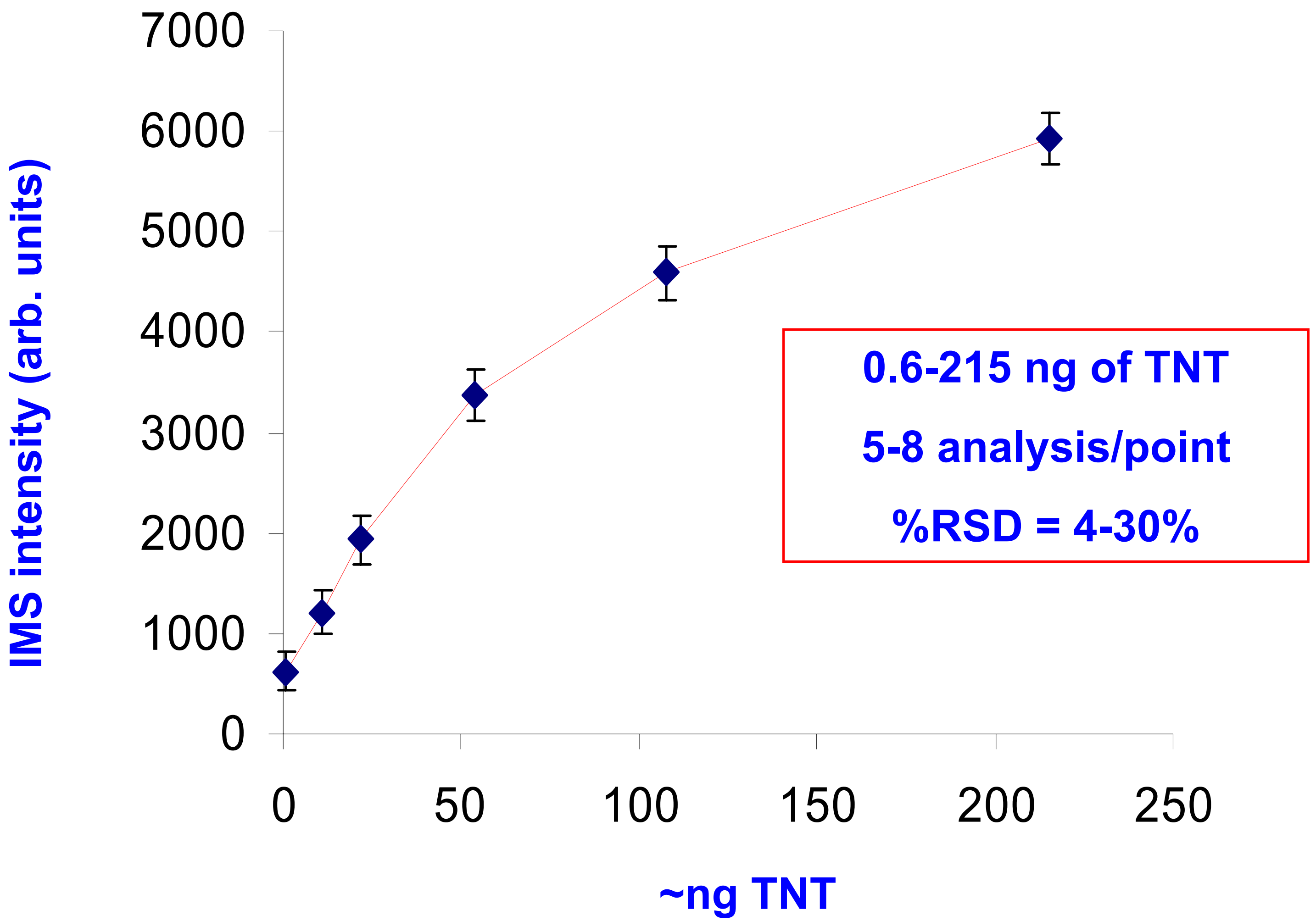
- All samples filtered with 0.2 μm filter to prevent plugging of inkjet tips.

Explosive Standard Preparation



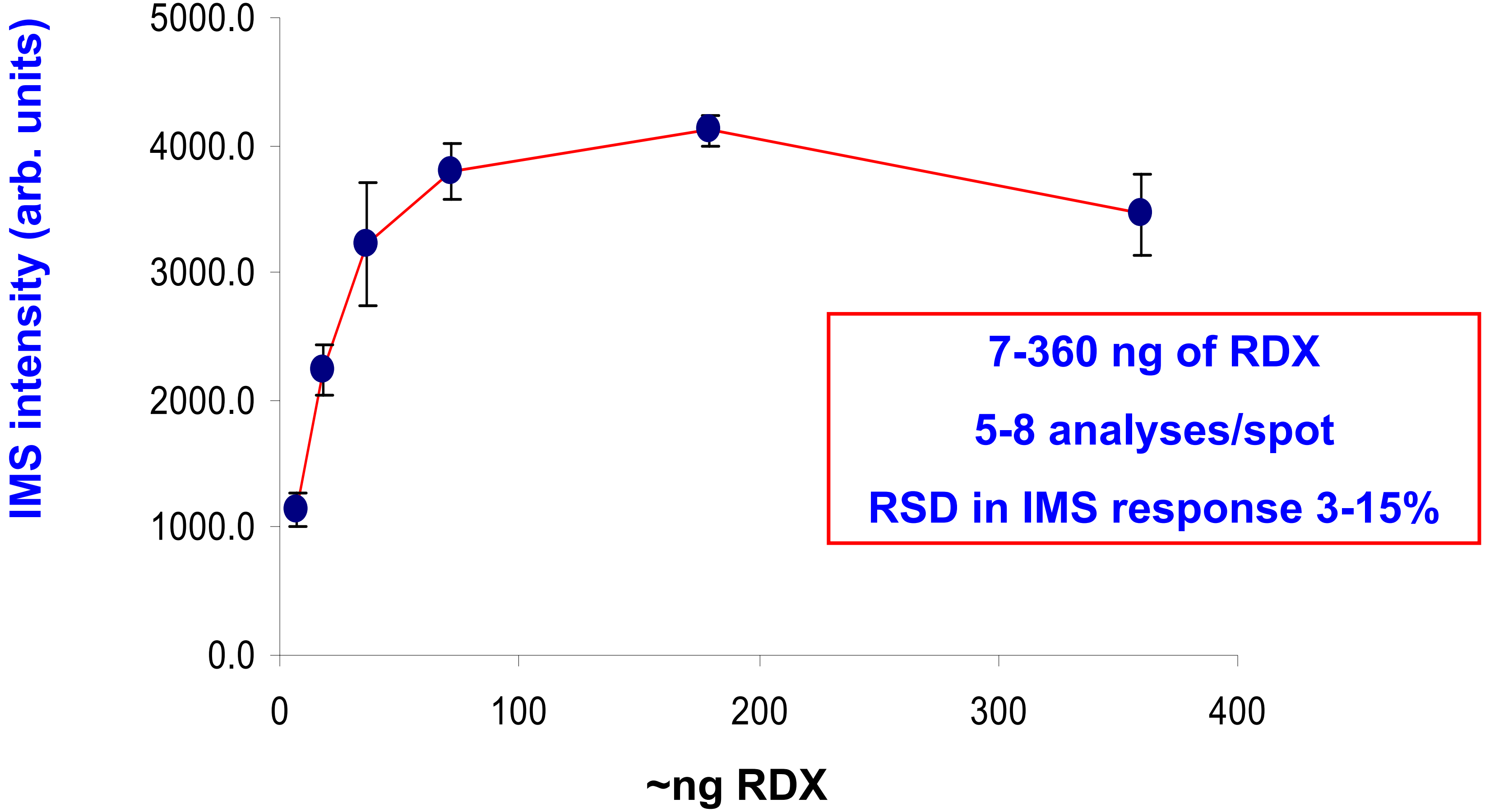
Calculated calibration curve for 120 μg/ml TNT standard solution in isobutanol with a 50 μm diameter jet orifice. Droplet size was assumed to be 60 μm in diameter. This gives 0.01357 ng/drop (13.57 pg /drop). Volume of each drop ~ 1.131×10^{-7} ml

Concentration Standards for IMS Response (TNT)



TNT printed directly on test swipes for IMS calibration

Concentration Standards for IMS Response (RDX)



RDX printed directly on test swipes for IMS calibration

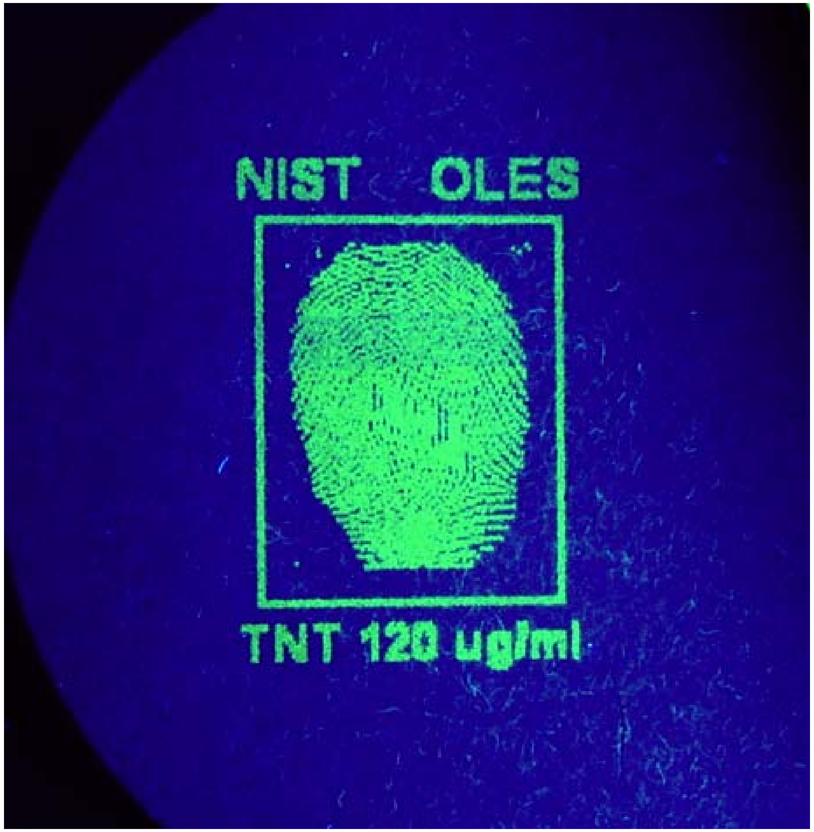
Ink-Jet Replication of a NIST Standard FingerPrint

Fingerprint image from NIST fingerprint image database

RDX + Fluorescien

- Convert fingerprint to binary image using Image Pro Plus Software.
- Transform image data to printer compatible format (comma delimited text files with x, and y position, fluid type, # drops)
- Dispense known number of drops/spot to create analyzable fingerprint.

Ink-Jet Created FingerPrint Composed of TNT and Fluorescein



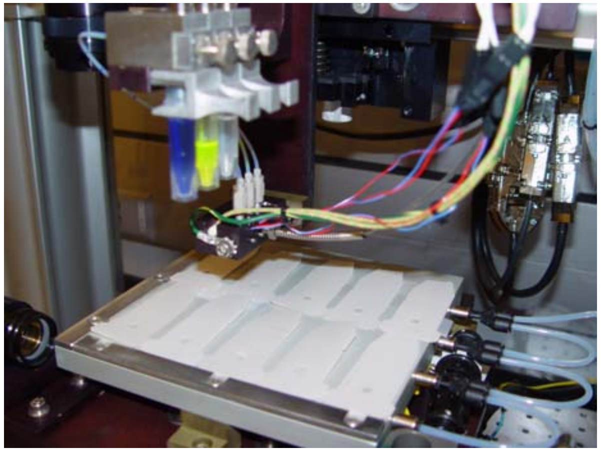
Printed fingerprint containing TNT and fluorescent dye

Standard solution 60 0ug/ml in isobutanal dilute with fluoroscien.

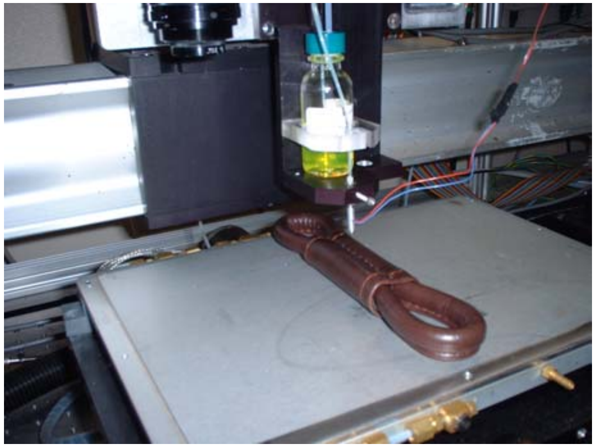
5789 drops x 5 drops/spot = 309 ng TNT

Inkjet Printing on Novel Test Surfaces

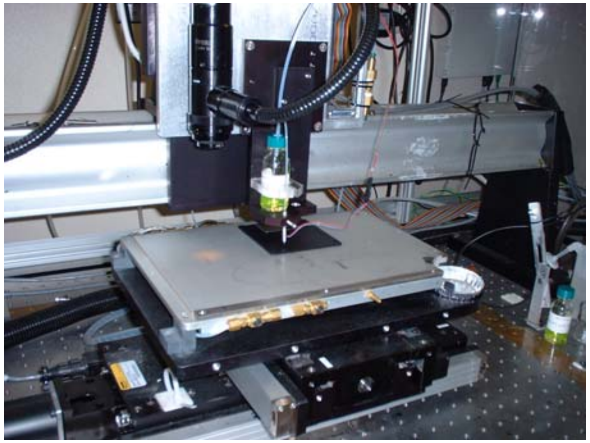
Non contact printing, large area x,y stage translation and adjustable z axis allows for printing of explosives standards on a variety of materials and non planar surfaces.



IMS Swipes



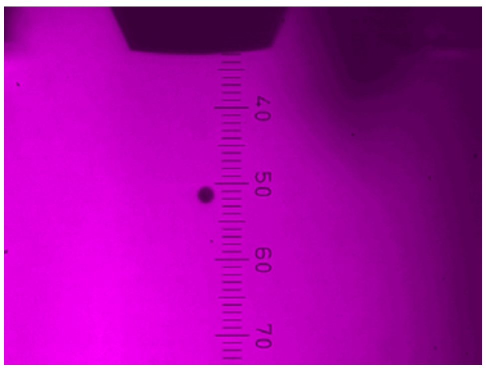
Luggage handles

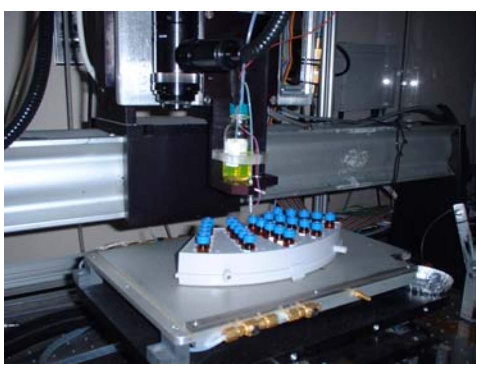


Floppy Disks

InkJet Drop Volume Calibration/Verification

Preparation of concentration standards depends critically on the accurate determination of the total amount of deposited explosive. This can be done in several ways:





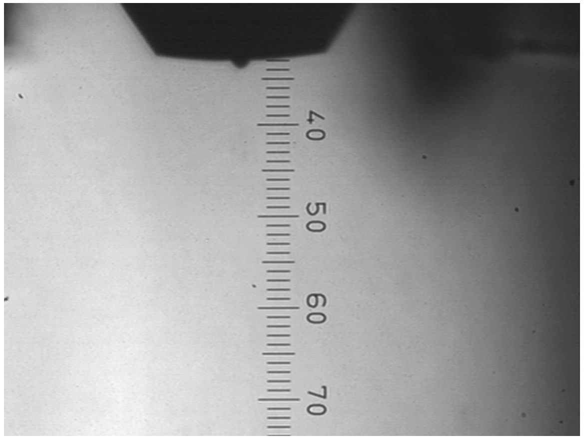
- Visual observation of droplet formation with strobe illumination. Volume calculation using image analysis.

- GC/MS analysis of mass of explosive in droplets. Jet samples into GC/MS autosampler sample vials.

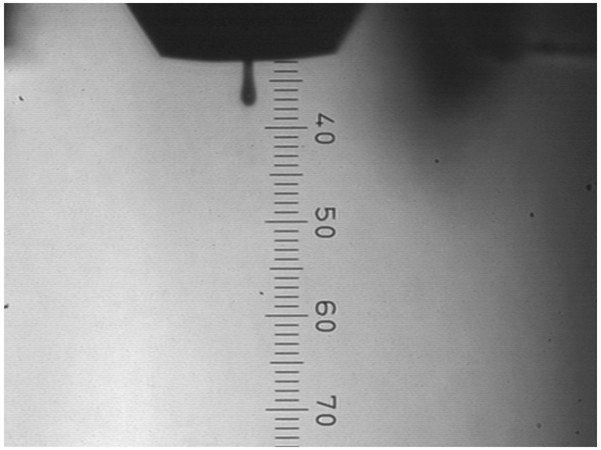
- Weighing multiple drops.

- Drop size on non wetting surface.

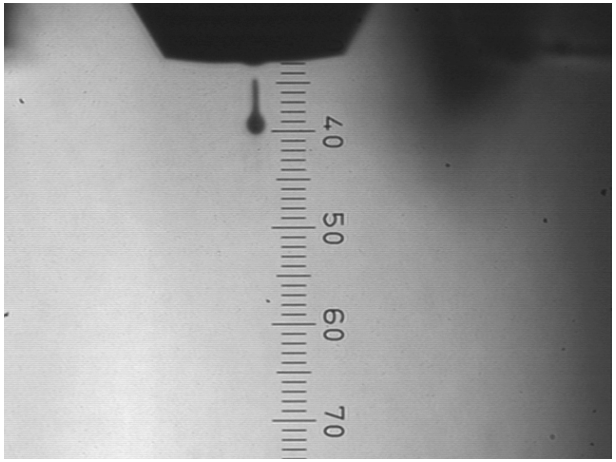
Droplet Ejection From Printer



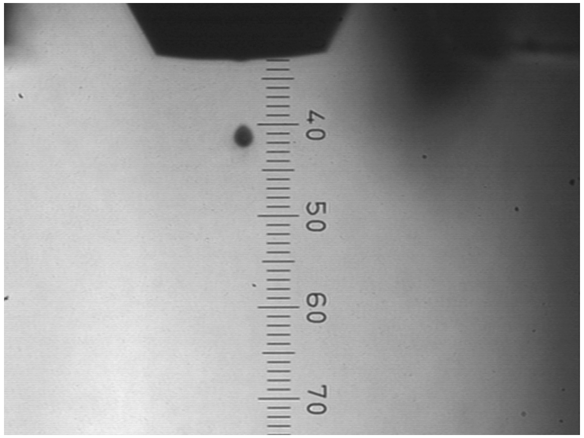
10 us



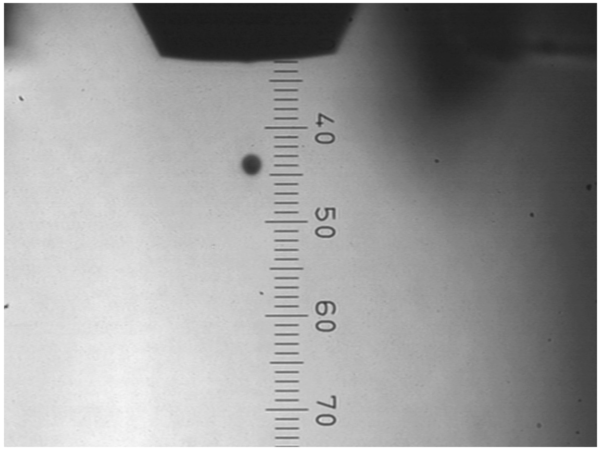
50 us



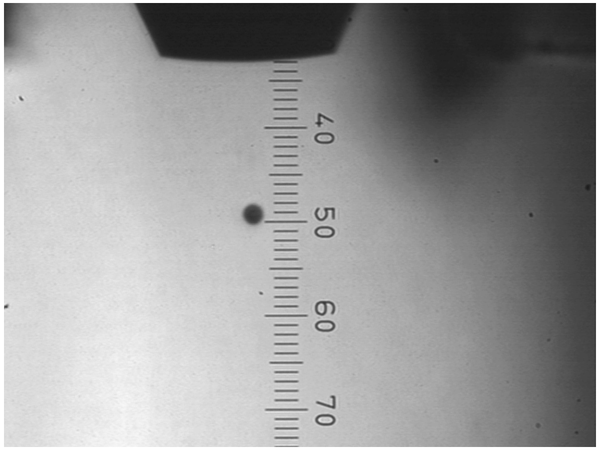
100 us



150 us



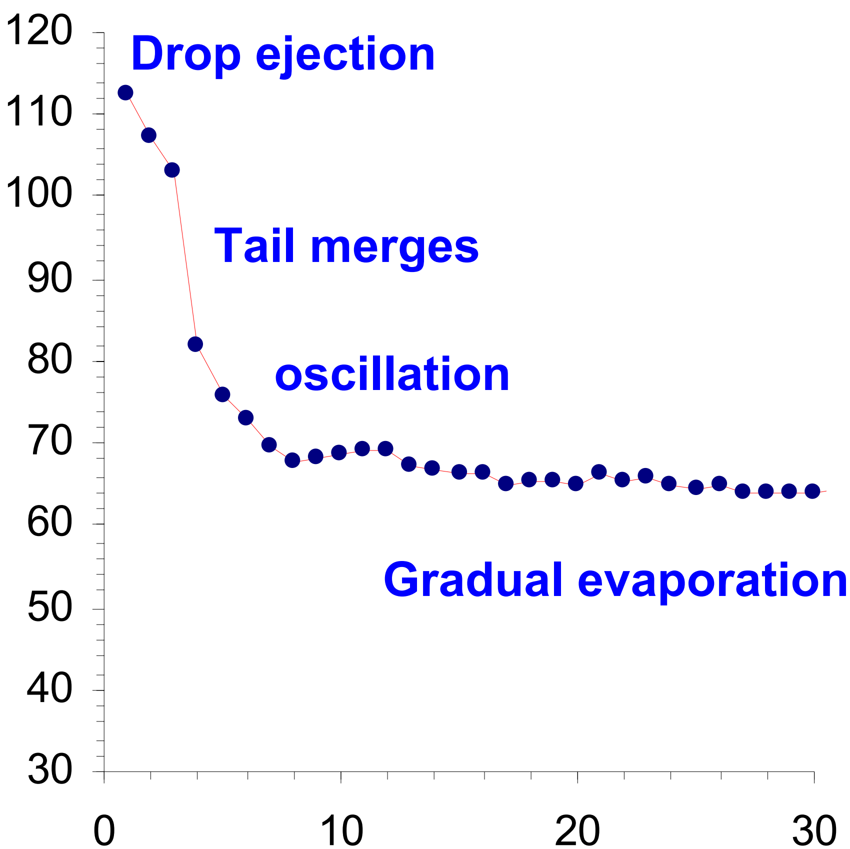
200 us

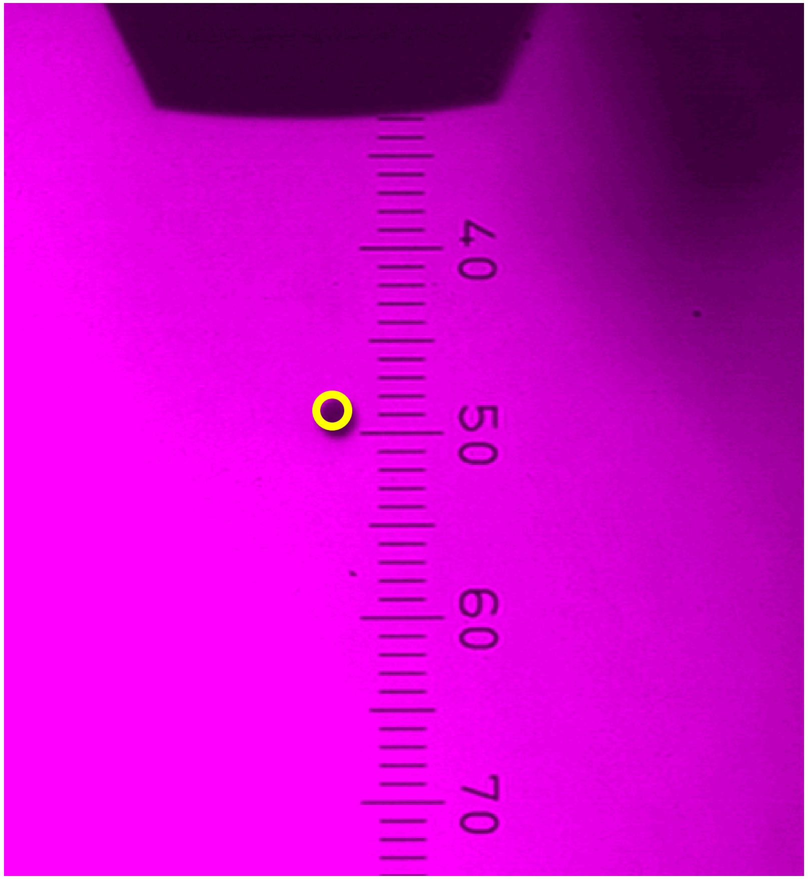


300 us

Displayed times represent time delay after initial ejection

Drop Diameter Calibration





Range 0-760 us elapsed time after drop ejection.

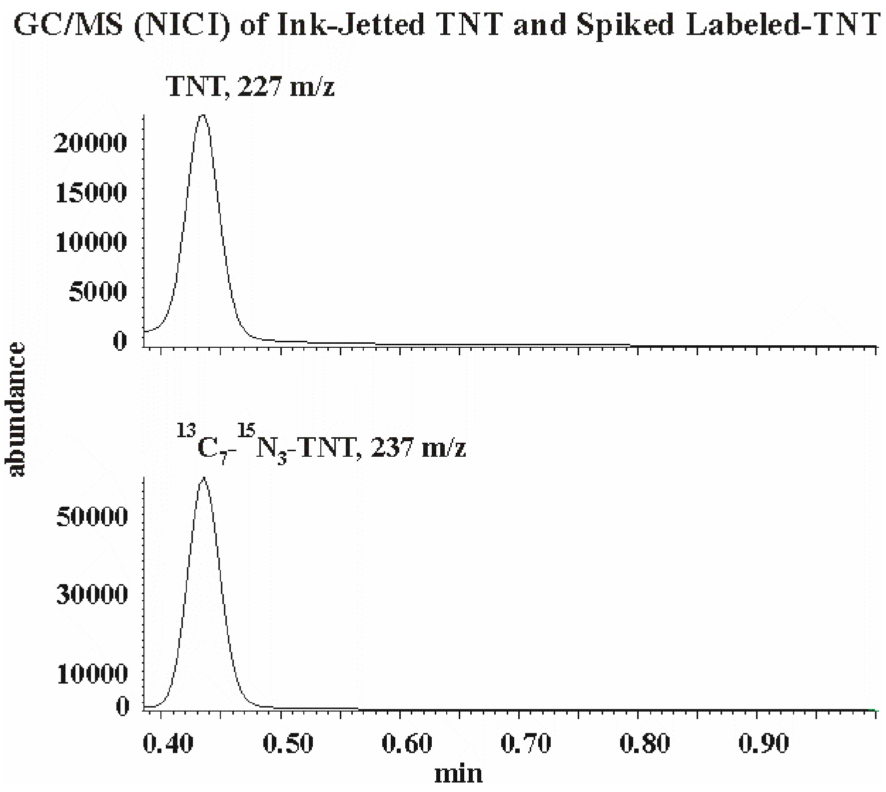
Average diameter 65.4 micrometers (average of frame 10-30)

GC/MS for Analysis of Inkjet Droplets Containing Explosives

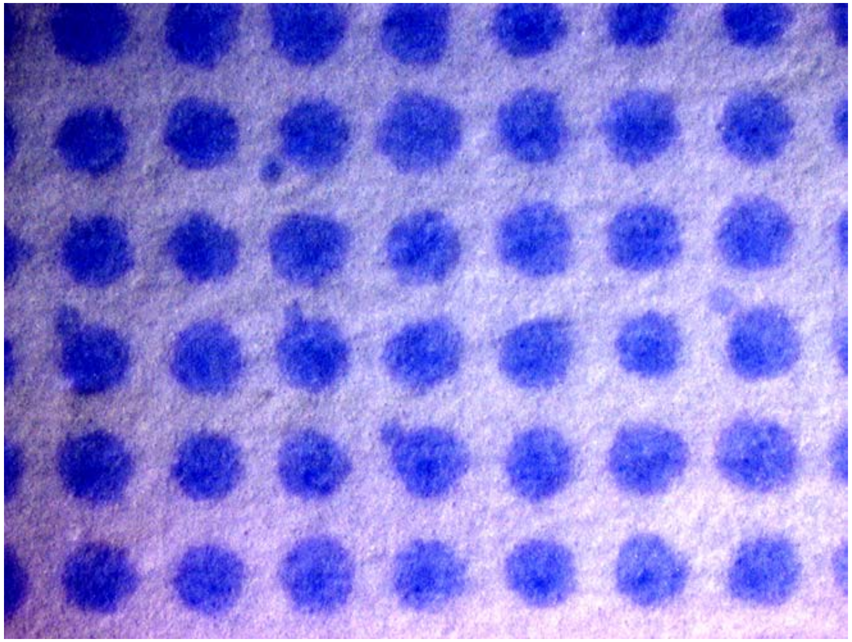
- This electron-capture mechanism most favorable Primary mechanism: $MX + e^{-}_{(thermal)} \Rightarrow MX^{\bullet -}$
- Selective for molecules containing heteroatoms (N, O, P, S, and Si).
- Use isotopically-labeled $^{13}C_7$-$^{15}N_3$-TNT for quantification.
- 1 m retention gap, 10 m x 0.22 mm HT5 GC column, 1 mL/min He flow.
- Methane as CI reagent, sim 227 and 237 m/z.

Gas Chromatography/Negative Ion Chemical Ionization Mass Spectrometry (GC/NICI-MS)

- Standard Deviation = 2.44%
- Relative Standard Deviation = 8.2%
- Conclusions: Preliminary data suggests printer is highly reproducible, precision less than 3% - need to evaluate multiple samples to confirm.



Quality Control of Standards



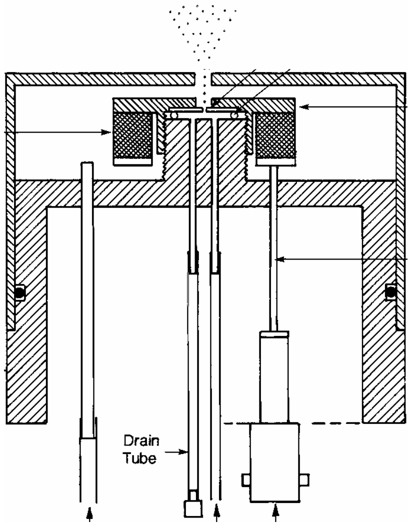
For routine observation of correct printer function, visual observation of droplet arrays using fluorescent or optical dyes is useful. This approach allows us to verify printhead misfires, satellite drop formation, tip plugging. Localizing deposit for anlalysts..

100 ug/ml of PETN Array with Ink….

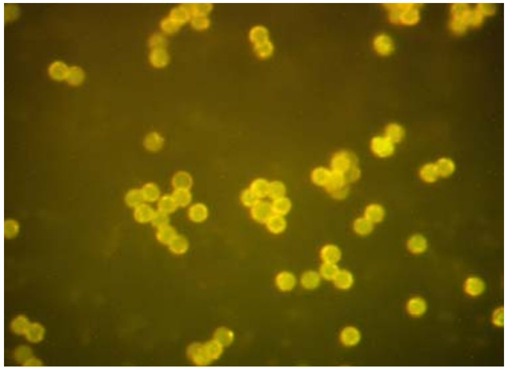
Looking for ideal ink or dye materials. Desirable qualities.

Stable to 200 oC for 30 seconds, no IMS background, minimal solvent, no particulates, visible in UV.

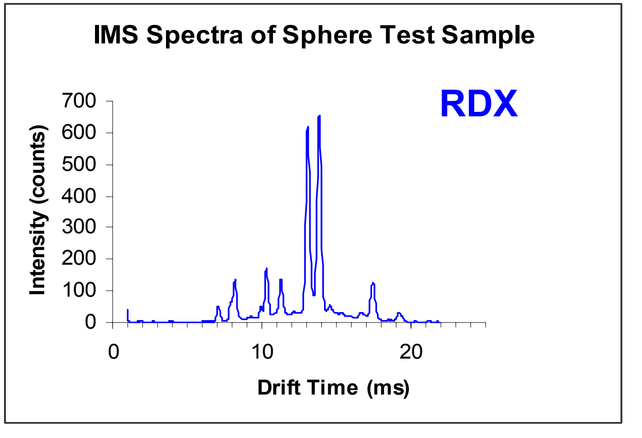
Another Approach? - Single Particle Explosive Standards



- Vibrating Orifice Particle Generator.
- Generate spheres of known and predicted size containing known amounts of explosive.
- Fluorescent tag added for visualization.
- Test explosives sampling procedures, particle release, portal collection.
- **Can do a first-principles verification of diameter**



Test explosive standard spheres
Nominal ~8 μm in diameter



Future Efforts: Refining the Metrology of InkJet Printing for Explosives

- Accurate drop size determination is important
  - Quantity of HE is dependent on solution concentration, individual drop size and number of identical drops
- Variation due to operating parameters (freq., pressure, wave strength…)
- Precision of drop formation
- Variations of drop size with different modes of operation (single vs burst)
- Drop-surface interactions (spreading, splattering, etc.)
- Q/A approaches to verifying drop diameter and delivery frequency
- Need to know Failure rate of printer
- Repeatability of performance – identical delivery (day to day)
- Useful solutions and solvents
- Plugging the jet/contamination problems
- Identification of sample spots-labeling
- Effects of taggants on IMS response
- Archive/lifetime of spots (how long are the samples viable)
- Surface incompatibilities
- Nature of sample geometry with respect to IMS

InkJet Printing of Explosive Standards

Preliminary Conclusions:

1. Feasibility of piezo electric inkjet printing of explosives demonstsrated
2. Preparation of concentration standards appears feasbile
3. Printing flexible approach for
4. Printing of patterns, finperprints is possible.

High throughput ~Assume 10,000 tabletop IMS instruments x 7 stds/day = 70,000 day * 365 = 25 million standards/year. Adding 6000 or so portal-based detection systems would require another 15 million standards/year.